

Adsorption of CO₂ on Molecular Sieves and Activated Carbon

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Received October 25, 2000. Revised Manuscript Received December 18, 2000

Pressure swing adsorption (PSA) and temperature swing adsorption (TSA) are some of the potential techniques that could be applicable for removal of CO₂ from high-pressure fuel gas streams. Molecular sieves and activated carbons are some of the sorbents that could be utilized in the PSA process. Volumetric adsorption studies of CO₂, N₂, or H₂ on molecular sieve 13X, molecular sieve 4A, and activated carbon were conducted at 25 °C up to a pressure of 300 psi (~2 × 10⁶ Pa). Preferential adsorption of CO₂ was observed with all three sorbents. The adsorption capacity of CO₂ for molecular sieve 13X was higher than that for molecular sieve 4A at all pressures up to 300 psi. At low pressures (<25 psi) the adsorption capacity for CO₂ of activated carbon was lower than that of molecular sieve 13X, but at higher pressures (>25 psi) activated carbon exhibited significantly higher CO₂ capacities than were found for molecular sieves. Competitive adsorption of CO₂ from gas mixtures also indicated that both molecular sieve 13X and activated carbon can be utilized for separation of CO₂ from gas mixtures.

Introduction

Fossil fuels supply more than 98% of the world's energy needs. However, the combustion of fossil fuels is one of the major sources of the greenhouse gas CO₂. It is necessary to develop technologies that will allow us to utilize the fossil fuels while reducing the emissions of greenhouse gases. Commercial CO₂ capture technology that exists today is very expensive and energy intensive. Improved technologies for CO₂ capture are necessary to achieve low energy penalties. Pressure swing adsorption (PSA) is one of the potential techniques that could be applicable for removal of CO₂ from gas streams.

PSA processes are based on preferential adsorption of the desired gas (e.g., CO₂) on a porous adsorbent at high pressure, and recovery of the gas at low pressure. Thus, the porous sorbent can be reused for subsequent adsorption. PSA technology has gained interest due to low energy requirements and low capital investment costs.^{1,2} Applications of PSA processes to separation/capture of carbon dioxide are also reported.^{3,4} Low recovery rate of CO₂ is one of the problems reported with the PSA processes. Development of regenerable sorbents that have high selectivity, high adsorption capacity, and high desorption rate for CO₂ adsorption/desorption is critical for the success of the PSA process.

In this work, three sorbents, namely, molecular sieve 13X, molecular sieve 4A, and activated carbon from Süd Chemie Inc., that can be utilized in the PSA process for recovery of CO₂ were studied. Volumetric adsorption studies of CO₂, N₂, and H₂ on the three sorbents were conducted at 25 °C and up to a pressure of 300 psi (~2 × 10⁶ Pa) to determine the equilibrium adsorption capacity of these materials. The adsorption isotherms of these materials at pressures up to 300 psi are not reported in the literature. Studies on competitive adsorption of CO₂ from gas mixtures were conducted utilizing an atmospheric micro reactor. Elemental characterizations of these sorbents were conducted utilizing advanced analytical techniques such as X-ray photoelectron spectroscopy and scanning electron microscopy/energy dispersive spectroscopy.

Experimental Section

The three sorbents, namely, Zeochem-Z10-02/molecular sieve 13X (8 × 12 mesh), Zeochem Z4-01/molecular sieve 4A (4 × 8 mesh), and G-32 H activated carbon (4 × 10 mesh), were obtained from Süd Chemie Inc. Adsorption isotherms at 25 °C of pure CO₂ (99.5%, Jackson Welding Supply Co.), N₂ (99.5%, Jackson Welding Supply Co.), and H₂ (99.95%, Butler Gas Products Co.) on the three sorbents were obtained up to an equilibrium pressure of about 300 psi (~2 × 10⁶ Pa) utilizing a volumetric adsorption apparatus. Approximately 10 mL of the sorbent materials were placed in the sample chamber and were evacuated to ~5 × 10⁻⁵ Torr. The amount of CO₂ adsorbed was calculated utilizing the pressure measurements before and after the exposure of the sample chamber to CO₂. Baseline data with CO₂ were obtained utilizing 10 mL of glass beads (2 mm diameter). Nine adsorption cycles were performed with each sorbent. After each cycle the sorbent was evacuated to about 5 × 10⁻⁵ Torr overnight.

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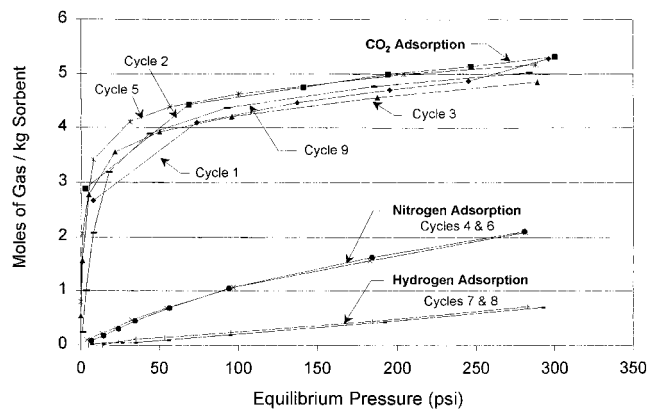


Figure 1. Adsorption isotherms of CO₂, N₂, and H₂ on molecular sieve 13X at 25 °C.

Cycles 1,2,3,4,7, and 10 were performed with CO₂, cycles 5 and 6 were performed with nitrogen, and cycles 8 and 9 were performed with hydrogen.

BET nitrogen surface areas of the materials were measured utilizing Micromeritics surface area and pore volume analyzer. X-ray photoelectron spectroscopy (XPS) spectra were recorded with a Physical Electronics Model SAM 590 equipped with a model 15-255 GAR analyzer and a 15 kV X-ray source from Physical Electronics.⁵ The system was routinely operated within a pressure range of 1.3×10^{-7} to 1.3×10^{-6} Pa (10^{-9} – 10^{-8} Torr). The instrument was calibrated using the photoemission lines $E_B(\text{Cu } 2p_{3/2}) = 932.4$ eV and $E_B(\text{Au } 4f_{7/2}) = 83.8$ eV. The binding energies were referenced to the C(1s) level at 284.6 eV for adventitious carbon. All intensities reported are experimentally determined peak areas divided by the instrumental sensitivity factors. Spectra were obtained with about five different samples and the intensity and binding energy values reported are the averages of values obtained from all sets of data. X-ray microanalysis was carried out using JEOL 840A model scanning electron microscope (SEM). The electron microscope is equipped with a Noran Instruments energy-dispersive spectrometer.⁶ The SEM was interfaced to a Noran Instruments Voyager-IV X-ray analysis and image processing unit. Resolution based on the Mn K α energy line was 149 eV.

The competitive adsorption studies at 25 °C were conducted utilizing Micromeritics Autochem 2910 atmospheric micro reactor. The composition of the two gas mixtures utilized were 14.8% CO₂ and 85.2% N₂, and 10% CO₂, 28% H₂, and 62% He. The analysis of the outlet gas stream was conducted utilizing a Pfeiffer Vacuum Thermostar mass spectrometer. The samples were pre-treated at 250 °C for 1 h in the micro reactor under helium prior to the exposure to the gas mixtures containing CO₂.

Results and Discussion

Adsorption Isotherms. Volumetric adsorption isotherms of CO₂, N₂, and H₂ on molecular sieve 13X at 25 °C are shown in Figure 1. The shape of the isotherms appears to be similar to type 1(Langmuir). The CO₂ adsorption increased rapidly when the pressure was increased up to 50 psi. The increase in CO₂ adsorption after 50 psi appears to be gradual. The adsorption isotherms for repeated cycles were very similar. This indicated that the adsorption is fully reversible and complete regeneration can be obtained by evacuation of the material after adsorption. At all pressures,

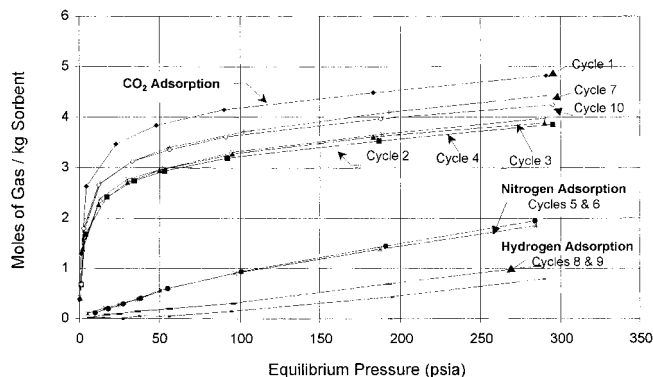


Figure 2. Adsorption isotherms of CO₂, N₂, and H₂ on molecular sieve 4A at 25 °C.

adsorption isotherms of both nitrogen and hydrogen were lower than those of CO₂. Both nitrogen and hydrogen isotherms were also completely reversible. Preferential adsorption of CO₂ on molecular sieve 13X indicates that this material can be used for separation of CO₂ from some gas mixtures. The final adsorption isotherm (cycle 9 which was obtained after the completion of adsorption experiments with nitrogen and hydrogen) was conducted with CO₂ and it was very similar to the previous adsorption isotherms with CO₂. This indicated that the sorbent was not affected by the adsorption of nitrogen and hydrogen.

The volumetric adsorption isotherms for molecular sieve 4A are shown in Figure 2. The adsorption isotherms indicate that the uptake of CO₂ was higher than that of the other two gases—nitrogen and hydrogen. This preferential uptake of CO₂ indicates that this sorbent may be suitable for the separation of CO₂ from gaseous mixtures. The adsorption isotherm of CO₂ for molecular sieve 4A during the first cycle was higher than that of the following cycles, indicating that the adsorption was not completely reversible. The adsorption at the first cycle was the highest. The average pore diameter of molecular sieve 4A is 4 Å, while the average pore diameter of molecular sieve 13X is about 10 Å. The kinetic diameter of the CO₂ molecule is 3.9 Å, which is only slightly lower than the pore diameter of molecular sieve 4A.⁷ So the mobility of the CO₂ molecule may be restricted inside the pores of molecular sieve 4A. The incomplete desorption of CO₂ after the first adsorption cycle in molecular sieve 4A may be due to the smaller pore size. However, the amount of CO₂ adsorbed was constant after the second cycle. This indicates that after the second cycle, a constant amount of CO₂ may be desorbed at each cycle. The uptake of CO₂ for molecular sieve 4A was lower than that of molecular sieve 13X at all equilibrium pressures up to 300 psi. However, both nitrogen and hydrogen adsorption isotherms of molecular sieve 4A appear to be similar to those of molecular sieve 13X. The adsorption of nitrogen and hydrogen did not appear to adversely affect the adsorption capacity of the sorbent for CO₂ adsorption.

The adsorption isotherms of CO₂ on activated carbon are shown in Figure 3. It is interesting to note that all the isotherms were extremely reproducible, which indicates the excellent reversibility of adsorption. The CO₂

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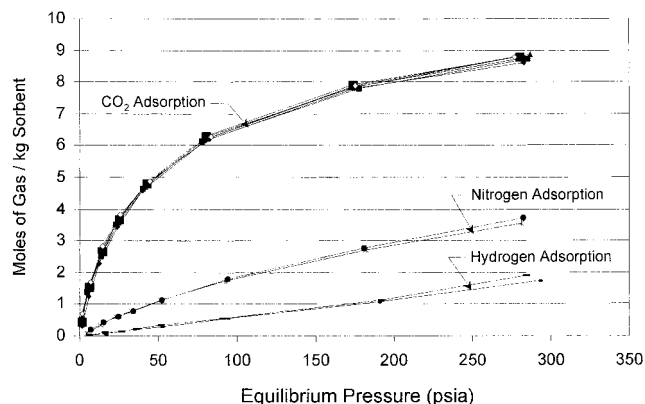


Figure 3. Adsorption isotherms of CO₂, N₂, and H₂ on activated carbon at 25 °C.

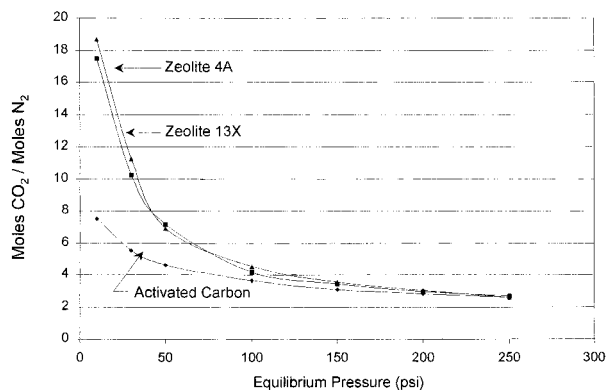


Figure 4. Ratios of amounts of CO₂/N₂ adsorption on three sorbents.

uptake of activated carbon was lower than that for the two molecular sieves at lower pressures (<30 psi), but at higher pressures the CO₂ uptake of activated carbon was higher than that of the molecular sieves. Nitrogen and hydrogen adsorption isotherms on activated carbon were also very reproducible. The final CO₂ adsorption cycle (cycle 10) was very similar to the first cycle, which indicated that the CO₂ adsorption capacity of the sorbent was not affected by the adsorption of other gases.

The ratio of the moles of adsorbed CO₂ to nitrogen is shown in Figure 4. The ratio of CO₂/nitrogen decreased with increasing pressure and appeared to remain constant above 150 psi in all three sorbents. This indicates that the selectivity of the sorbents for CO₂ adsorption is better at lower pressures even though the total CO₂ adsorption was higher at higher pressures. At lower pressures, this selectivity molar ratios appears to be higher for the molecular sieves than that for the activated carbon but was similar at higher pressures. Similar observations were made with the adsorbed mole ratios of CO₂/hydrogen on the three sorbents.

Adsorption isotherms of CO₂ (best isotherm selected from the repeated cycles) with adsorption denoted in mol/kg and mol/L, for three adsorbents are shown in Figures 5 and 6, respectively. Both molecular sieves 13X and 4A exhibited higher uptake of moles of CO₂ per kg of the sorbent at pressures less than 30 psi, but at higher pressures activated carbon showed higher CO₂ uptake. When the CO₂ uptake was in mol/L, the activated carbon showed higher CO₂ uptake at pressures above 100 psi.

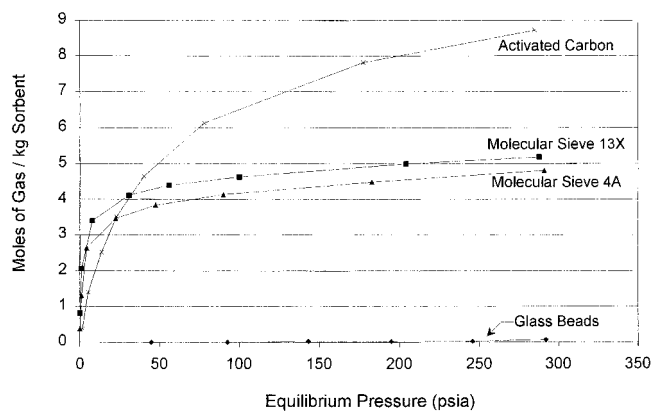


Figure 5. Adsorption isotherms of CO₂ on three sorbents at 25 °C.

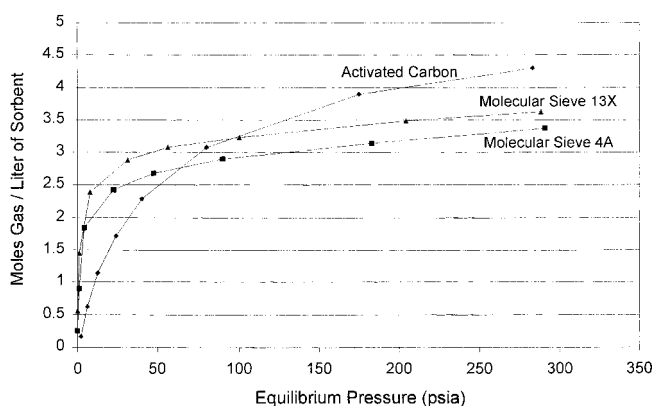


Figure 6. Adsorption isotherms of CO₂ on three sorbents at 25 °C.

Isosteric heats of adsorption as a function of surface coverage were calculated using adsorption isotherms at different temperatures (30, 40, 50 °C). The Clausius–Clapeyron equation was utilized in these calculations.⁸ Isosteric heats of adsorption of molecular sieve 13X decreased from 50 to 10 kJ mol⁻¹ with increasing coverage from 1 to 5 mol/kg. For the activated carbon, the isosteric heats of adsorption decreased from 28 to 11 kJ/mol with increasing coverage. The wide range of activation energies observed for the molecular sieve 13X indicated that there is a wide range of sites with varying adsorption energies present in molecular sieve 13X.

Characterization of Adsorbents. Since molecular sieve 13X and activated carbon showed reversible adsorption most of the characterization work was done with these two sorbents. The nitrogen BET surface areas of molecular sieves 13X and activated carbon were 506 and 897 m²/g, respectively. The high surface area of activated carbon may have contributed to the high CO₂ uptake at higher pressures. The CO₂ uptake values per unit surface area are shown in Figure 7. It is interesting to note that the moles of CO₂ adsorbed per unit area is higher on molecular sieve 13X than that on activated carbon. These values were similar on both materials only at about 250–300 psi. This indicates that the surface of molecular sieve 13X has a better affinity for CO₂ than that of activated carbon.

The cross sectional area⁹ of the CO₂ molecule is 19.5 Å². If close packing of CO₂ is assumed, at a monolayer

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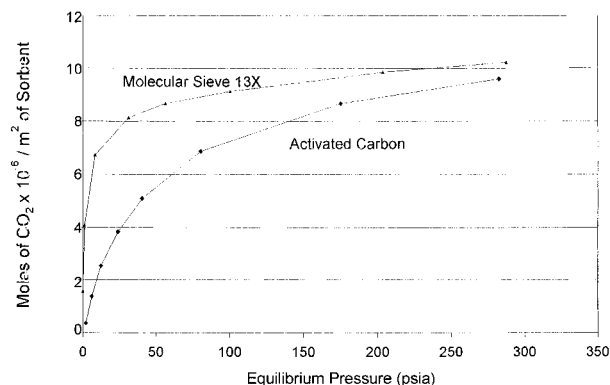


Figure 7. Adsorption isotherms of CO₂ at 25 °C based on the surface area of the sorbents.

Table 1: Elemental Ratios at the Bulk and the Surface

	bulk 13X	surf. 13X	bulk 4a	surf. 4a		bulk act. C	surf. act. C
Al/Si	0.75	1.08	0.77	0.74	Al/C	0.0001	0.023
Na/Si	0.60	0.69	0.54	0.78	Na/C	0.001	0.005
K/Si	0.004	0.03	0.04	0.04	K/C	0.007	0.041

coverage the surface should occupy about 8.5×10^{-6} mol/m². From the adsorption isotherms it was determined that the molecular sieve 13X has about 9.9×10^{-6} moles of CO₂ per square meter at saturation coverage (250–300 psi) and this is very close to the value corresponding to a close packed monolayer coverage of CO₂. The saturation CO₂ coverage of activated carbon as determined by the adsorption isotherms is about 9.5

$\times 10^{-6}$ mol/m². This indicates that a close pack monolayer of CO₂ is also formed at saturation with the activated carbon. So both these materials utilize the complete surface area to form a close packed monolayer at higher pressures.

The skeletal and bulk densities of molecular sieve 13X as measured by mercury porosimetry were 1.87 and 1.06 g/cm³, respectively, and for activated carbon these values were 1.14 and 0.94 g/cm³, respectively. So the density of activated carbon was lower than that of the molecular sieve 13X.

The elemental analysis of the bulk and the surface of the sorbents are listed in Table 1. The major elements observed at the surface of the molecular sieves were Si, Al, and Na. Trace amounts of K, Ca, and Fe were also observed. The ratio of the K/Si of molecular sieve 13X was considerably higher at the surface than that at the bulk. This indicates that most of the K resides on the surface of the molecular sieve 13X. Surface analysis of the activated carbon indicated that there were Al, K, and trace amounts of Cl, Na, S, and Si on the surface. Both Al/Si and K/Si ratios were substantially higher at the surface of activated carbon than at the bulk as shown in Table 1. This indicated that the potassium resides mainly on the surface of the activated carbon, similar to the observations with molecular sieve 13X. Elemental distributions of the cross sections of the pellet of molecular sieve 13X are shown in Figure 8. It is clear that all the elements including the trace elements are well distributed in the pellet. Since the chemical com-

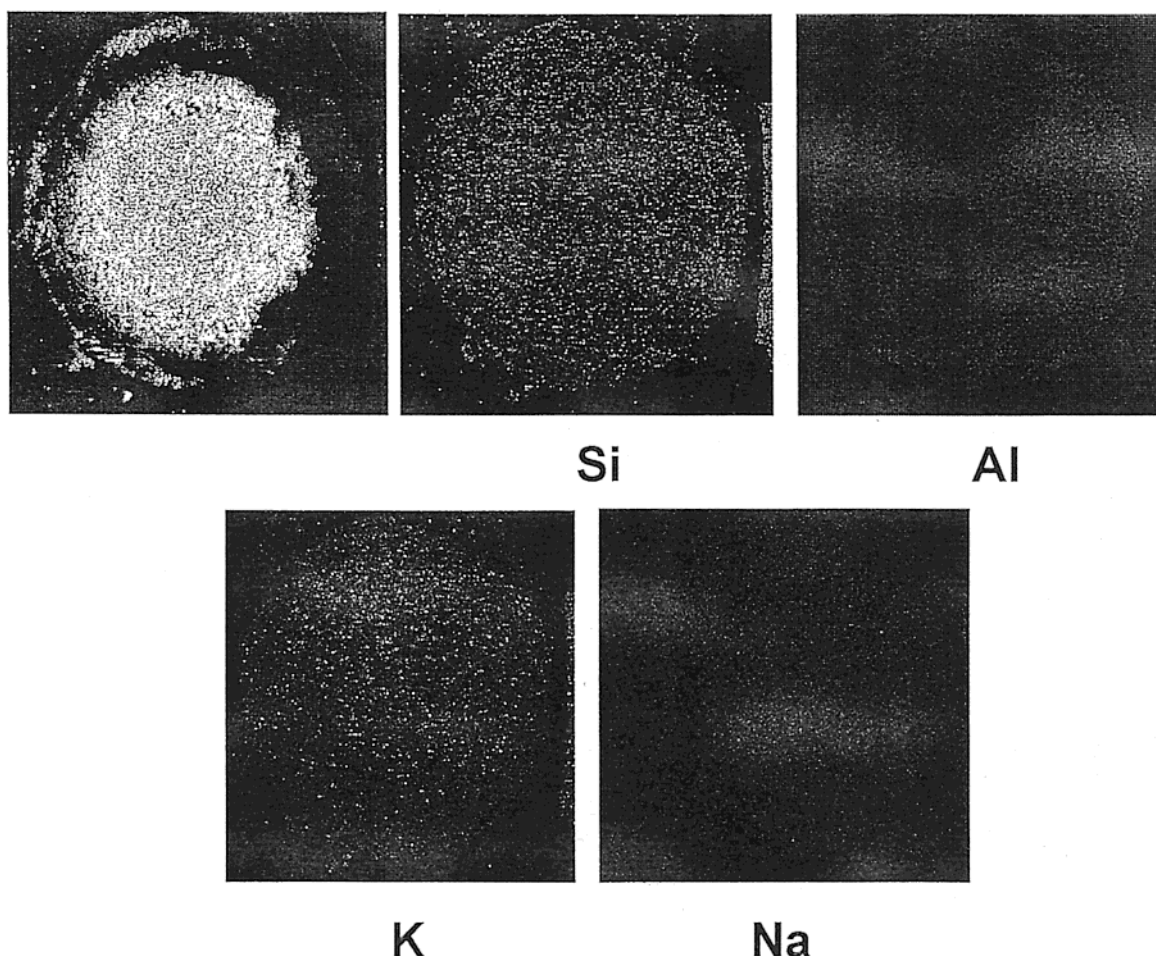


Figure 8. Elemental maps of fresh molecular sieves.

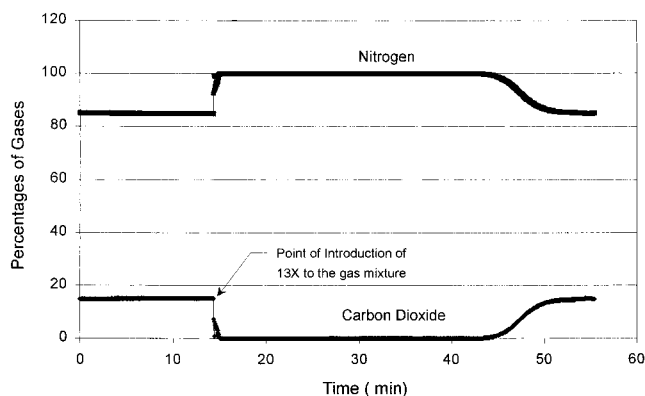


Figure 9. Micro reactor studies on CO₂ separation with molecular sieve 13X— 14.8% CO₂/85.2% N₂ mixture.

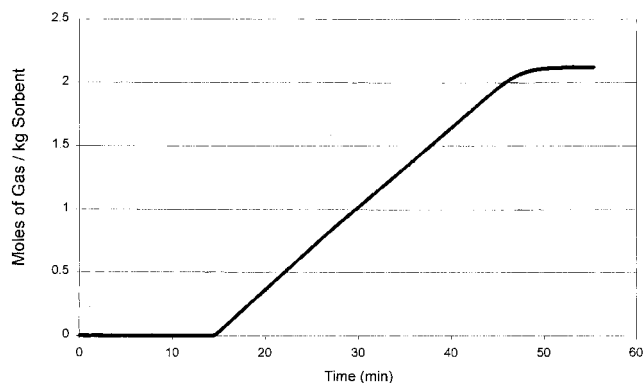


Figure 10. Amount of CO₂ adsorption from CO₂/N₂ mixture as a function of time on molecular sieve 13X.

positions of molecular sieve 13X and activated carbon are completely different, it is difficult to relate the adsorption properties to the chemical composition of the surfaces.

Competitive Adsorption Studies from Gas Mixtures Containing CO₂. Results of the competitive gas adsorption studies conducted utilizing 14.8% CO₂ and 85.2% N₂ on molecular sieve 13X in the atmospheric micro reactor are shown in Figure 9. The gas mixture was introduced to 1.5 g of molecular sieve 13X at a flow rate of 15 cm³/min and at 25 °C. After the introduction of the gas mix to the molecular sieve 13X, the CO₂ concentration decreased to almost zero while the nitrogen concentration increased to 100%, until the breakthrough. This indicates that an excellent separation of CO₂ from a gas mixture of N₂ and CO₂ can be obtained with molecular sieve 13X. The amount of CO₂ adsorbed per kilogram of the sorbent as a function of time, calculated from the data is shown in Figure 10. There is a linear uptake of CO₂ with time and the total amount of CO₂ adsorbed at the breakthrough or saturation was about 2.1 mol/kg of the sorbent. This value is very similar to the amount of CO₂ adsorbed at 1 atm from volumetric equilibrium adsorption studies, as shown in Figure 1. This indicates that the full capacity of the molecular sieve 13X was utilized for CO₂ adsorption during competitive gas adsorption from a CO₂ and N₂ mixture. A similar observation was made with molecular sieve 13X during competitive CO₂ adsorption from

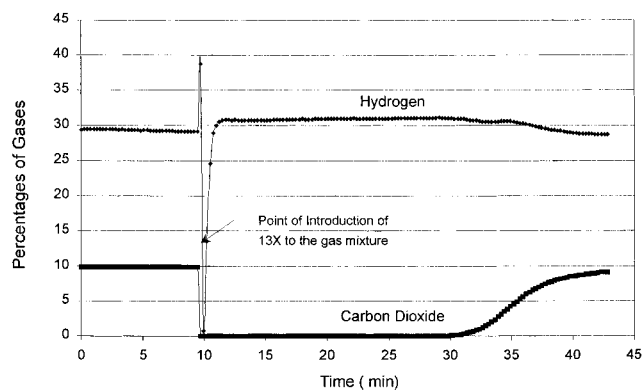


Figure 11. Micro reactor studies on CO₂ separation with molecular sieve 13X (10% CO₂/28% H₂/62% He mixture).

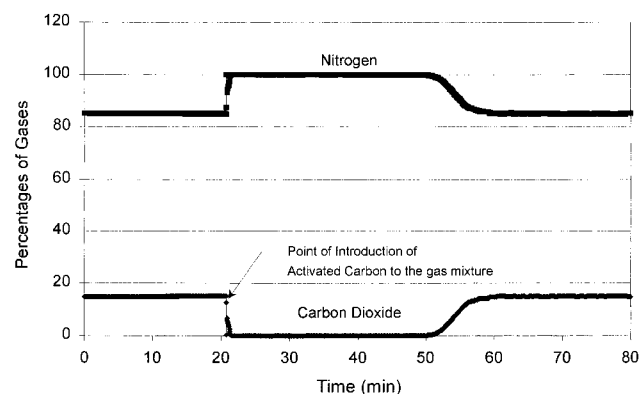


Figure 12. Micro reactor data on CO₂ separation with activated carbon—14.8% CO₂/85.2% N₂ mixture.

a gas mixture containing 10% CO₂, 28% H₂, and 62% He as shown in Figure 11. It was also possible to obtain an excellent separation of CO₂ from the gas mixture containing 14.8% CO₂ and 85.2% N₂, with activated carbon (0.5 g) as shown in Figure 12, but it was necessary to lower the flow rate (5 cm³/min) to increase the contact time to utilize the full equilibrium adsorption capacity for CO₂ adsorption. This indicates that the rate of adsorption of CO₂ on activated carbon at 1 atm was lower than that for the molecular sieve 13X.

Conclusions

Molecular sieve 13X, 4A, and activated carbon showed preferential adsorption of CO₂ at 25 °C and pressures up to 300 psi. Adsorption of CO₂ was found to be reversible on both molecular sieve 13X and activated carbon. Equilibrium adsorption data from volumetric adsorption experiments indicated that the amount of CO₂ adsorbed on the molecular sieves is more than that of activated carbon at pressures less than 50 psi, but activated carbon showed significantly higher adsorption than molecular sieves at pressures above 50 psi. The equilibrium adsorption capacities of activated carbon, molecular sieve 13X, and molecular sieve 4A at 300 psi and at 25 °C are about 8.5, 5.2, 4.8 mol of CO₂/kg of the sorbent, respectively. At 300 psi, both molecular sieve 13X and activated carbon utilized the full capacity of the surface to form a close packed monolayer at the surface. Isosteric heats of adsorption calculations indicated that the molecular sieve 13X has a wide distribution of active sites for CO₂ adsorption. Potassium is

preferentially distributed at the surface of the molecular sieve 13X and activated carbon. Excellent separation of CO₂ was obtained from gas mixtures containing both CO₂ /N₂ and CO₂ /H₂/He utilizing both molecular sieve 13X and activated carbon during competitive gas adsorption studies performed with the micro reactor. However, it was necessary to use higher contact times

of the gases with activated carbon than that with molecular sieve 13X to achieve the excellent separation.

Acknowledgment. The Authors thank Mr. Bill Turner at Süd Chemie Inc. for providing the sorbents for this work.

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